Chapter 21

CATALYTIC EFFECTS OF Ni-HUMIC COMPLEXES ON THE REDUCTIVE DEHALOGENATION OF C_1 AND C_2 CHLORINATED HYDROCARBONS

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21.1. INTRODUCTION

The redox chemistry of humic substances (HSs) is important in many processes relevant to the fate and transport of contaminants in terrestrial and aquatic environments. In particular, the role of HSs in the abiotic and microbially mediated transformation of organic and inorganic contaminants is of great current interest. Humic substances can serve as electron donors and terminal electron acceptors for microbial anaerobic respiration [1-5], as reductants for organic and inorganic contaminants [6-8], and as electron transfer mediators [9-11].

Although anoxic environments often are sufficiently reducing for the reductive transformation of many contaminants to be thermodynamically favorable, the transfer of electrons from reduced species to a given contaminant is often kinetically limited, resulting in slow transformation rates *in situ*. However, in the presence of materials that can act as electron transfer mediators, such as bacterial transition-metal coenzymes (e.g., vitamin B_{12} [Co], coenzyme F_{430} [Ni], and hematin [Fe]), rates for reductive dehalogenation reactions can be greatly enhanced [12-20]. In addition, several low-molar mass quinones, dissolved organic matter (DOM), and HSs are known to be effective electron mediators for the reduction of nitroaromatics, dioxins and chlorinated aliphatic hydrocarbons by reduced sulfur species, Ti^{III} citrate, or Fe^{II}_{aq} [9-11,19,21,22]. The ability of HSs to act as electron transfer mediators has generally been attributed to the presence of quinone groups within their structures [9,10,23-25]. However, HSs complex a wide range of transition metals, and recently DOM- and HS-transition metal complexes (specifically Ni and Cu complexes) have been shown to facilitate the reductive dechlorination of trichloroethene (TCE) by

Ti^{III} citrate [26-28], suggesting that HS-transition metal complexes may also contribute to the electron transfer capacity of HSs.

This paper examines the ability of HS-Ni complexes to mediate the reduction of chlorinated methanes, ethanes, ethenes and ethynes in homogeneous aqueous solutions with Ti^{III} citrate as the bulk reductant. Reaction rates, products, and potential pathways are presented.

21.2. MATERIALS AND METHODS

21.2.1. Chemicals and Reagents

Hexachloroethane (HCA, 99%), pentachloroethane (PCA, 95%), 1,1,2,2-tetrachloroethane (1122TeCA, 99%), 1,1,2-trichloroethane (112TCA), tetrachloroethene (or perchloroethene (PCE), 99.9+%), TCE (99.5%), 1,1-dichloroethene (11DCE, 99%), cis-1,2-dichloroethene (c12DCE, 97%), trans-1,2-dichloroethene (t12DCE, 98%), chloromethane (CM, 99.5%), sodium citrate dihydrate (99%), nickel(II) chloride hexahydrate (99.9999%), Aldrich humic acid (AHA), propene (99+%), 1-butene (99+%), and a mixture of cis- and trans-2-butene (38.1% cis and 61.6% trans) were obtained from Aldrich. Tetrachloromethane (or carbon tetrachloride (CT), 99%) and 1,1,1,2-tetrachloroethane (1112TeCA, 99%) were purchased from Chem Service. Titanium(III) chloride (15% in HCl) and 1,1-dichloroethane (11DCA, >97%) were obtained from Fluka. Dichloromethane (DCM, spectroscopic grade), trichloromethane (or chloroform (CF), HPLC grade), and 1,1,1-trichloroethane (111TCA, purified) were purchased from Fisher. A multi-component gas mix containing methane, ethane, ethene, and acetylene (each at 1.0 mole percent in N$_2$); chloroethene (or vinyl chloride (VC), 0.1% in N$_2$); propane (1.002% in N$_2$); and n-butane (1.0% in N$_2$) were purchased from Scott Specialty Gases. Tris (Trizma® base, 99.9%), and 1,2-dichloroethane (12DCA, reagent grade) were obtained from Sigma and J.T. Baker, respectively. Chloroacetylene (CAc), synthesized as described by Arnold and Roberts [29], was generously provided by Dr. Lynn Roberts' laboratory.

Aldrich HA was treated extensively to remove residual fulvic acids and inorganic impurities including metals [30]. Briefly, AHA was dissolved in 10^{-2} M NaOH and then treated with HF/HCl and Na saturated Na-Chelex 100 (Bio-Rad Laboratories). Excess Na was removed by placing the AHA solution in 1000 Da molar mass cutoff (MWCO) cellulose ester dialysis tubing and dialyzing against 18 MΩ–cm water.

Titanium(III) citrate (250 mM) was prepared in a glove box containing an atmosphere of 4-6% H$_2$ in N$_2$ with a modified literature method [31]. Briefly, 7.35 g of trisodium citrate and 4.0 g of Trizma® base were dissolved in 25 mL of deoxygenated 18 MΩ–cm water. The solution was placed in an ice bath with continuous stirring, and 15 mL of 15% TiCl$_3$ in HCl was added, followed by 3.2 mL of 50% NaOH (w/w) to raise the pH to ~8.0 at 25°C. This stock solution oxidizes over a period of several hours and thus was prepared fresh for each experimental run.

21.2.2. Methods

Experimental Setup. The experimental system consisted of 160-mL serum vials, each with 90 mL of aqueous phase consisting of AHA at a concentration of 11.1 mg of organic carbon (OC) L^{-1} or 18 MΩ–cm water (for controls without AHA). The solutions were spiked with 1.0 mL of 10 mM Ni^{2+} in 0.1 M HCl (or 1.0 mL of 0.1 M HCl for controls without Ni) and 0.1 mL of 1 M NaOH. After 24 h, 3 mL of 2.0 M Tris (adjusted to pH 8.0) and 6 mL of 250 mM Ti^{III} citrate were added and the vials were sealed with aluminum crimp caps with Teflon-lined rubber septa. The E_h of systems containing Ti^{III} citrate was initially -700 mV as measured with a Pt redox electrode. Vials were spiked with 5 μL of a 1.0 M methanolic solution of *n*-heptane (added as an internal standard). Unless otherwise indicated, all preparative work was performed in a glove box with an atmosphere of 4-6% H_2 in N_2 or under continuous Ar sparging.

Reactions were initiated by spiking the vials with 5 μL of a 1.0 M methanolic solution of a given chlorinated hydrocarbon with the exception of PCA and HCA systems, which were spiked with 50 μL of 0.1 M methanolic solutions, and CM systems, which were spiked with 120 μL of CM gas at STP. Experimental systems were prepared in duplicate. Initial solution concentrations were AHA at 10 mg OC L^{-1}, 100 μM Ni^{2+}, 100 mM Tris, and 15 mM Ti^{III} citrate; the total mass of chlorinated hydrocarbon in each vial was 5 μmol. Experiments were conducted at 20°C, and the systems were kept well mixed either by placement on a roller drum that rotated vertically while the bottle axis remained horizontal, or by vigorous shaking by hand (for reactions with half-lives of less than 5 min). At selected intervals, 100-μL headspace samples were removed from the serum vials and analyzed for the parent compound and transformation product concentrations.

Analytical Methods. Nonchlorinated hydrocarbons; CAc; chloroethenes; mono-, di-, and trichloroethanes; and chloromethanes (except CT) were analyzed with a Hewlett-Packard 5890 Series II gas chromatograph equipped with a GSQ column (0.53 mm id by 30 m) and a flame ionization detector (FID, 200°C). Samples were injected in split mode at 180°C. Helium was used as the carrier gas at a flow rate of 4.7 mL min^{-1}, with the split vent at 9.7 mL min^{-1}. The oven temperature was held at 50°C for 2 min, ramped at 25°C min^{-1} to 200°C, and held for 10 min at 200°C. Carbon tetrachloride and tetra-, penta-, and hexachloroethane were analyzed with a DB-1 column (0.53 mm id by 30 m) and an FID (200°C). Samples were injected in split mode at 200°C. The carrier gas was He at 7.7 mL min^{-1} with the split vent at 5.2 mL min^{-1}. Carbon tetrachloride was analyzed under isothermal conditions at 50°C. The oven temperature for 1112TeCA and 1122TeCA was held at 60°C for 1.2 min, ramped at 30°C min^{-1} to 100°C, and held for 2.5 min at 100°C; for PCA the oven temperature was held at 60°C for 1 min, ramped at 30°C min^{-1} to 150°C, and held at 150 °C for 1 min; and for HCA the oven temperature was ramped from 90°C to 180°C at 30°C min^{-1} then held at 180°C for 1 min. The system was calibrated by equilibrating known masses of analytes and internal standard *n*-heptane in serum vials containing the same ratio of aqueous phase to vapor phase as in the experimental systems, thus accounting for water-vapor partitioning.

Experiments to detect low-yield intermediates in the reduction of TCE and PCE were performed as described above, except that TCE and PCE loadings were higher (150 μmol). Headspace samples for these experiments were analyzed with a Hewlett Packard 5890 gas chromatograph equipped with a Hewlett Packard 5971 mass-selective (MS) detector. Samples were injected splitless at 150°C onto a 0.32 mm id by 30 m GSQ-PLOT column. The oven temperature was held at 40°C for 3 min, ramped at 25°C min^{-1} to 200°C, and held at 200°C for 8 min. The detector temperature was 280°C. To avoid swamping the detector, the acquisition parameters were set with a 3-min initial solvent delay, and the MS was placed offline for the time interval corresponding to the elution window of the internal standard (*n*-heptane). Selected ion monitoring (SIM) methods were used for CAc and dichloroacetylene with target ions of M^+, M^{+2} and M^{+4}.

Analysis of carbon monoxide in headspace samples was performed with a Trace Analytical (Menlo Park, CA) RGA3 Reduction Gas Analyzer with an oven temperature of 266°C. Formate was analyzed with a Dionex LC20 ion chromatograph with self-regenerating suppressor control. An IONPAC AG11 guard column (4 × 50 mm) and an IONPAC AG11 analytical column (4 × 250 mm) were used with a weakly basic eluent (NaOH, 350 μmol L^{-1}) at a flow rate of 1.0 mL min^{-1}.

Kinetic Analysis. Apparent pseudo-first-order rate constants (k_{obs}) were obtained by fitting the data for the mass of parent chlorinated hydrocarbon in the system over time to Eq. 21.1,

$$M_{CH_t} = M_{CH_0} e^{-k_{obs} t} \qquad (21.1)$$

where t is time and M_{CHt} and M_{CH0} are the masses of chlorinated hydrocarbon in the system at times t and zero, respectively. For a reaction taking place in the solution phase only, the apparent pseudo-first-order rate constant that pertains to the reaction of a volatile constituent capable of rapid partitioning between the solution phase and the headspace (k_{obs}) is equivalent to the rate constant that would be obtained in a headspace-free system (k'_{obs}), as described by Burris et al. [12]. Values of k'_{obs} were calculated with "dimensionless" Henry's law constants for 11DCA, 111TCA, VC, 11DCE, c12DCE, t12DCE, TCE, PCE, CF, and CT from Gossett [32]; 112TCA, 1112TeCA, and 1122TeCA from Tse et al. [33]; PCA from Mackay and Shiu [34]; HCA from Pankow et al. [35]; acetylene and ethene from Burris et al. [13]; and CAc from Semadeni et al. [36].

21.3. RESULTS AND DISCUSSION

21.3.1. Reaction Kinetics

The reduction of chlorinated ethynes, ethenes, and ethanes was markedly enhanced in the presence of Ni-AHA complexes (as shown for VC in Figure 21.1), an observation that is consistent with earlier reports that Ni-DOM complexes (including Ni-HS complexes) are effective electron transfer mediators for the reductive dehalo-
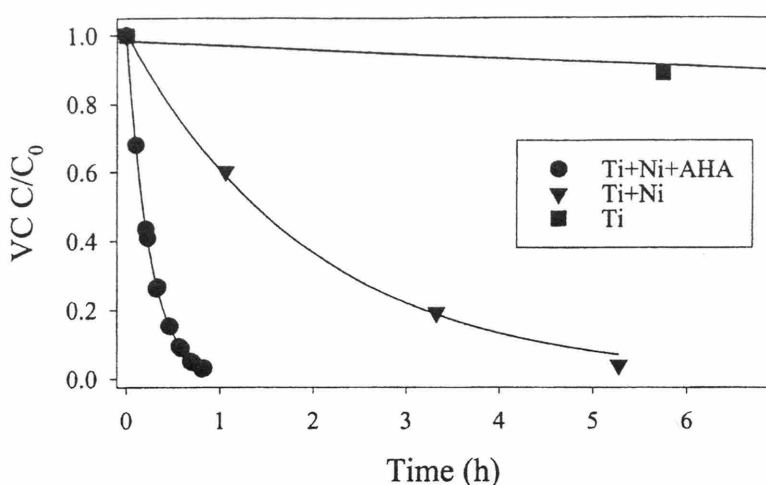
Figure 21.1 Reduction of VC in systems containing 10 mg OC L^{-1} AHA, 100 μM Ni^{2+}, 100mM Tris, 15 mM Ti^{III} citrate, and 5 μmol VC as indicated. Plots are of data from duplicate vials. Curves represent first-order fits to the data.

genation of TCE with Ti^{III} citrate as the bulk electron source [26-28]. The reduction of chlorinated hydrocarbons (i.e., those for which reduction was observed) in our experimental systems was well described by pseudo-first-order kinetics, as shown for VC (Figure 21.1). Apparent pseudo-first-order rate constants (k'_{obs}), the coefficients of determination, adjusted for the number of degrees of freedom (adj r^2), and reaction half-lives ($t_{1/2}$) are listed in Table 21.1. Although most chlorinated hydrocarbons were reduced in the presence of Ti^{III} citrate alone, the reduction rate was much higher in the presence of Ni-AHA complexes, while a more moderate enhancement was observed in systems containing Ni without AHA. The reduction of chlorinated hydrocarbons in the presence of Ti^{III} citrate and AHA was the same as with Ti^{III} citrate alone (data not shown), indicating that AHA in the absence of added Ni was not an effective electron transfer mediator for these reactions.

21.3.2. Reaction Products and Pathways

General Observations. The reduction of the parent chlorinated hydrocarbons typically resulted in fully dechlorinated products (Table 21.2). Loss of analytes due to sorption on the Teflon-lined septa and volatilization from the serum vials was minimal (< 5%) over the time scale of these experiments (typically less than 2 d, but no longer than 14 d); thus, the incomplete carbon recovery observed for many of the compounds suggests the possible formation of products that are not identifiable by our analytical methods (e.g., compounds with relatively low volatility). The results for individual compounds are discussed in the following sections.

Chlorinated Methanes. The reduction of CT initially resulted in the formation of CF, which was subsequently reduced to DCM, CM, carbon monoxide, methane, and a suite of C_2-C_4 nonchlorinated alkanes and alkenes (ethane, ethene, propane, propene, *n*-butane, 1-butene, and *cis*- and *trans*-2-butene) (Table 21.2). Volatile products accounted for approximately 71% and 69% of the carbon introduced as CT and CF, respectively (per mole C), two-thirds of which were nonchlorinated hydrocarbons (primarily methane). Approximately 29% and 31% of the carbon added to the system as CT and CF was not accounted for in the mass balance of the identified products; sorption of the identified products to components of the reaction vessel and

Table 21.1. Apparent pseudo-first-order rate constants (k'_{obs}) and half-lives for the reductive transformation of chlorinated methanes, ethynes, ethenes, and ethanes.

Compound	System	k'_{obs} (s^{-1})	adj r^2	t$_{1/2}$ (min)
Methanes Chloromethane	Ti+Ni+AHA	NR[a]		
(CM)	Ti+Ni	NR		
	Ti	NR		
Dichloromethane	Ti+Ni+AHA	NR		
(DCM)	Ti+Ni	NR		
	Ti	NR		
Chloroform	Ti+Ni+AHA	$3.74(\pm0.17)^b \times 10^{-4}$	0.950	41
(CF)	Ti+Ni	$7.98(\pm0.28) \times 10^{-5}$	0.994	145
	Ti	$6.30(\pm1.01) \times 10^{-6}$	0.794	1830
Carbon Tetrachloride	Ti+Ni+AHA	$2.23(\pm0.08) \times 10^{-2}$	0.992	0.52
(CT)	Ti+Ni	$6.44(\pm0.35) \times 10^{-3}$	0.983	1.8
	Ti	$5.44(\pm0.21) \times 10^{-3}$	0.991	2.1
Ethynes Acetylene	Ti+Ni+AHA	$4.51(\pm0.07) \times 10^{-3}$	0.997	2.6
	Ti+Ni	$8.51(\pm0.19) \times 10^{-4}$	0.998	14
	Ti	$1.12(\pm0.11) \times 10^{-4}$	0.970	103
Chloroacetylene	Ti+Ni+AHA	$5.48(\pm0.25) \times 10^{-3}$	0.997	2.1
(CAc)	Ti+Ni	$8.97(\pm0.44) \times 10^{-4}$	0.991	13
	Ti	$1.12(\pm0.11) \times 10^{-4}$	0.991	26
Ethenes Ethene	Ti+Ni+AHA	$7.88(\pm0.63) \times 10^{-5}$	0.969	146
	Ti+Ni	$4.63(\pm0.09) \times 10^{-5}$	0.999	249
	Ti	$4.06(\pm0.41) \times 10^{-7}$	0.998	28400
Vinyl Chloride	Ti+Ni+AHA	$1.27(\pm0.046) \times 10^{-3}$	0.968	9.1
(VC)	Ti+Ni	$2.16(\pm0.12) \times 10^{-4}$	0.997	53
	Ti	$3.13(\pm0.52) \times 10^{-6}$	0.893	3690
1,1-Dichloroethene	Ti+Ni+AHA	$7.45(\pm0.11) \times 10^{-4}$	0.996	16
(11DCE)	Ti+Ni	$2.74(\pm0.14) \times 10^{-5}$	0.993	422
	Ti	$6.49(\pm0.80) \times 10^{-6}$	0.957	1780
cis-1,2-Dichloroethene	Ti+Ni+AHA	$6.11(\pm0.28) \times 10^{-4}$	0.971	18
(c12DCE)	Ti+Ni	$1.70(\pm0.023) \times 10^{-4}$	0.999	68
	Ti	$5.43(\pm0.51) \times 10^{-6}$	0.958	2130
trans-1,2-Dichloroethene	Ti+Ni+AHA	$4.13(\pm0.16) \times 10^{-4}$	0.976	28
(t12DCE)	Ti+Ni	$2.30(\pm0.01) \times 10^{-4}$	0.999	50
	Ti	$1.47(\pm0.22) \times 10^{-5}$	0.958	784

Table 21.1. Continued.

Compound	System	k'_{obs} (s^{-1})	adj r^2	$t_{1/2}$ (min)
Trichloroethene	Ti+Ni+AHA	$6.34(\pm0.46) \times 10^{-4}$	0.949	18
(TCE)	Ti+Ni	$3.96(\pm0.39) \times 10^{-5}$	0.949	292
	Ti	$9.40(\pm0.89) \times 10^{-6}$	0.949	1230
Tetrachloroethene	Ti+Ni+AHA	$1.08(\pm0.038) \times 10^{-4}$	0.946	107
(PCE)	Ti+Ni	$8.12(\pm0.48) \times 10^{-6}$	0.986	1420
	Ti	$1.70(\pm0.11) \times 10^{-6}$	0.981	6800
Ethanes Chloroethane	Ti+Ni+AHA	NR		
(CA)	Ti+Ni	NR		
	Ti	NR		
1,1-Dichloroethane	Ti+Ni+AHA	$3.58(\pm0.42) \times 10^{-7}$	0.865	32200
(11DCA)	Ti+Ni	NR		
	Ti	NR		
1,2-Dichloroethane	Ti+Ni+AHA	NR		
(12DCA)	Ti+Ni	NR		
	Ti	NR		
1,1,1-Trichloroethane	Ti+Ni+AHA	$1.33(\pm0.13) \times 10^{-3}$	0.884	8.7
(111TCA)	Ti+Ni	$6.08(\pm0.37) \times 10^{-4}$	0.992	19
	Ti	$8.07(\pm0.76) \times 10^{-5}$	0.969	143
1,1,2-Trichloroethane	Ti+Ni+AHA	$2.51(\pm0.18) \times 10^{-5}$	0.965	460
(112TCA)	Ti+Ni	$7.63(\pm0.25) \times 10^{-6}$	0.990	1510
	Ti	NR		
1,1,1,2-Tetrachloroethane	Ti+Ni+AHA	$1.25(\pm0.85) \times 10^{-2}$	0.981	0.93
(1112TeCA)	Ti+Ni	$5.74(\pm0.26) \times 10^{-3}$	0.992	1.9
	Ti	$5.71(\pm0.18) \times 10^{-3}$	0.996	2.1
1,1,2,2-Tetrachloroethane	Ti+Ni+AHA	$1.90(\pm0.075) \times 10^{-4}$	0.972	61
(1122TeCA)	Ti+Ni	$4.64(\pm0.23) \times 10^{-5}$	0.978	249
	Ti	$8.23(\pm0.70) \times 10^{-6}$	0.939	1400
Pentachloroethane	Ti+Ni+AHA	$2.44(\pm0.31) \times 10^{-2}$	0.983	0.47
(PCA)	Ti+Ni	$9.54(\pm1.08) \times 10^{-3}$	0.967	1.2
	Ti	$7.58(\pm0.38) \times 10^{-3}$	0.991	1.5
Hexachloroethane	Ti+Ni+AHA	$3.75(\pm0.47) \times 10^{-2}$	0.991	0.31
(HCA)	Ti+Ni	$1.50(\pm0.17) \times 10^{-2}$	0.985	0.77
	Ti	$2.01(\pm0.19) \times 10^{-2}$	0.994	0.57

[a]Non-reactive; [b]Rate constant ± standard error.

Table 21.2. Initial transformation reactions and products, observed intermediates, terminal products, and carbon recovery from the Ni-AHA-mediated reductive transformation of chlorinated methanes, ethynes, ethenes, and ethanes.

Compound	Initial reduction reaction and product	Observed intermediates	Terminal products[a]	Carbon recovery[b]
Methanes				
CF	Unknown	unknown	methane (38%), CO[c] (2%), DCM (16%), CM (6%), C$_2$-C$_4$ hydrocarbons (7%)	69%
CT	hydrogenolysis→ CF	CF	methane (34%), CO (2%), DCM (10%), CM (3%), C$_2$-C$_4$ hydrocarbons (22%)	71%
Ethynes				
Ac[d]	bond reduction→ EE[e]	EE	EE & EA[f] (79%), C$_3$-C$_6$ hydrocarbons (15%)	94%
CAc	hydrogenolysis→ Ac	Ac, VC, EE	EE & EA (77%), C$_3$-C$_6$ hydrocarbons (15%)	92%
Ethenes				
Ethene	bond reduction→ EA		EE (4%), EA (94%)	98%
VC	hydrogenolysis→ EE	EE	EE & EA (95%)	95%
11DCE	α-elimination→ EE	EE	EE & EA (89%), C$_3$-C$_6$ hydrocarbons (9%)	98%
c12DCE	hydrogenolysis→ VC β-elimination→ Ac	VC, Ac, EE	EE & EA (92%), C$_3$-C$_6$ hydrocarbons (5%)	97%
t12DCE	hydrogenolysis→ VC β-elimination→ Ac	VC, Ac, EE	EE & EA (89%), C$_3$-C$_6$ hydrocarbons (9%)	98%
TCE	hydrogenolysis→ c/t12DCE hydrogenolysis→ 11DCE β-elimination→ CAc	c/t12DCE, 11DCE, CAc, Ac, VC, EE	EE & EA (72%), C$_3$-C$_6$ hydrocarbons (14%)	86%
PCE	hydrogenolysis→ TCE β-elimination→ DCAc	TCE, DCAc,[g] EE	EE & EA (78%), C$_3$-C$_6$ hydrocarbons (11%)	89%
Ethanes				
11DCA	α-elimination→ EA hydrogenolysis→ CA		EA (5%), 11DCA (92%), CA (1%)	98%

Table 21.2. Continued

Compound	Initial reduction reaction and product	Observed intermediates	Terminal products[a]	Carbon recovery[b]
111TCA	hydrogenolysis→ 11DCA	11DCA, EE	EE & EA (30%)	98%
	α-elimination→ CA		C₃-C₆ hydrocarbons (2%)	
			11DCA (14%) CA (52%)	
112TCA	β-elimination→ VC	VC, EE	EE & EA (90%)	90%
1112TeCA	β-elimination→ 11DCE	11DCE, EE	EE & EA (87%), C₃-C₆ hydrocarbons (6%)	93%
1122TeCA	β-elimination→ c/t12DCE	c/t12DCE, VC, EE	EE & EA (89%), C₃-C₆ hydrocarbons (3%)	92%
PCA	β-elimination→ TCE	TCE, EE	EE & EA (76%), C₃-C₆ hydrocarbons (13%)	89%
HCA	β-elimination→ PCE	PCE, TCE, EE	EE & EA (79%), C₃-C₆ hydrocarbons (11%)	90%

[a]Including, where appropriate, unreacted parent compound; [b]Percent of C derived from parent compound recovered as identified products and unreacted parent compound; [c]Carbon monoxide; [d]Acetylene; [e]Ethene (EE); [f]Ethane (EA); [g]Suspected but not confirmed.

loss due to leakage from the reaction vessels were minimal, suggesting that there are other significant products that are not detected by our analytical methods.

The initial step in the reduction of halogenated hydrocarbons is commonly reported to be a single electron transfer with the concerted or stepwise cleavage of the C-Cl bond resulting in the formation of a radical [37-42]. For CT, this process results in the formation of a trichloromethane radical [43-45] that is unstable and can react by several mechanisms, including 1) accepting a second electron and abstracting a proton to form CF; 2) coupling with a second trichloromethane radical, forming HCA; and 3) accepting a second electron with the subsequent loss of an additional chlorine, forming dichlorocarbene. Chloroform was observed as the principal initial product of CT reduction; however, traces of carbon monoxide were also observed, which may indicate the formation of a dichlorocarbene (or carbenoid) intermediate; dichlorocarbene reacts readily with water to form carbon monoxide and formic acid [46]. Formate was not present at detectable levels (i.e., > 2 µM) in any of our experiments. However, Robinson [47] showed that carbon monoxide is the primary product of the reaction of dichlorocarbene with water and that formate is produced by a subsequent (and slower) reaction of carbon monoxide with hydroxide. In addition to reduction of trichloromethyl radicals, dichlorocarbene may also be produced by the hydrolysis of CF [46], which likely accounts for the carbon monoxide formed during the reduction of CF.

The reduction of CT and CF to methane may result from a series of sequential replacements of hydrogen for chlorine, such that CT $\rightarrow$ CF $\rightarrow$ DCM $\rightarrow$ CM $\rightarrow$ methane. However, experiments independently examining the reduction of DCM and CM showed that neither DCM nor CM was reduced over the time scale of the experiments. Moreover, once formed from the reduction of CT or CF, DCM and CM concentrations remained stable, indicating that these compounds are not intermediates in the Ni-AHA mediated reduction of CT and CF to methane. Thus, the formation of methane from the reductive dehalogenation of CT and CF must result from processes other than sequential hydrogenolysis.

Castro and Kray [40] have proposed a pathway for the reduction of CT to methane by Cr^{II} in aqueous solution that does not require DCM and CM intermediates. The proposed pathway involves a series of single electron transfers in which chloromethyl radicals accept an electron with the subsequent loss of a chlorine, forming the corresponding carbene/carbenoid, which can then be reduced to a methyl radical containing one less chlorine atom (Figure 21.2). The process can be repeated until the last chlorine is removed, resulting in carbene, which can be reduced to a methane radical and finally to methane via the stepwise transfer of two electrons and two protons. Although such a reaction scheme does not involve DCM or CM as an intermediate, these species may be formed by terminal side reactions in which dichloromethane radicals or chloromethane radicals accept an additional electron while abstracting a proton.

Chlorinated Ethynes. The reduction of CAc in our experimental systems was extremely rapid. Acetylene was the dominant product of the reduction of CAc mediated by Ni-AHA complexes, indicating that reduction of CAc occurs primarily via

hydrogenolysis. Chloroacetylene was also reduced to VC, though to a much smaller extent. The terminal products of CAc reduction mediated by Ni-AHA complexes (that is, ethane, ethene, and C_3-C_6 alkenes and alkanes) are consistent with the products observed for the reduction of acetylene and VC (as described in the following section). Acetylene and VC have been reported as products of CAc reduction by both Zn^0 [29] and vitamin B_{12} with Ti^{III} citrate [36]. However, VC was not observed as an intermediate in the reduction of CAc by Fe^0 [48]. The formation of C_3-C_6 hydrocarbons was observed during the reduction of CAc by Fe^0 [48], but not in CAc reduction by Zn^0 [29] or cobalamin [36].

Acetylene was rapidly reduced to ethene, which was subsequently reduced to ethane, though at a much lower rate. In addition to ethene and ethane, the reduction of acetylene was accompanied by formation of longer-chained (C_3-C_6) alkenes and alkanes, primarily n-butane, 1-butene, cis-2-butene, and trans-2-butene. Independent experiments examining the reduction of ethene revealed that ethane is the only product of ethene reduction in our experimental system, indicating that the formation of C_3-C_6 alkene and alkane products from reduction of acetylene and CAc occurs prior to the reduction of ethene. The formation of C_3-C_6 hydrocarbons also has been observed during the reduction of acetylene by Fe^0 in aqueous sys-
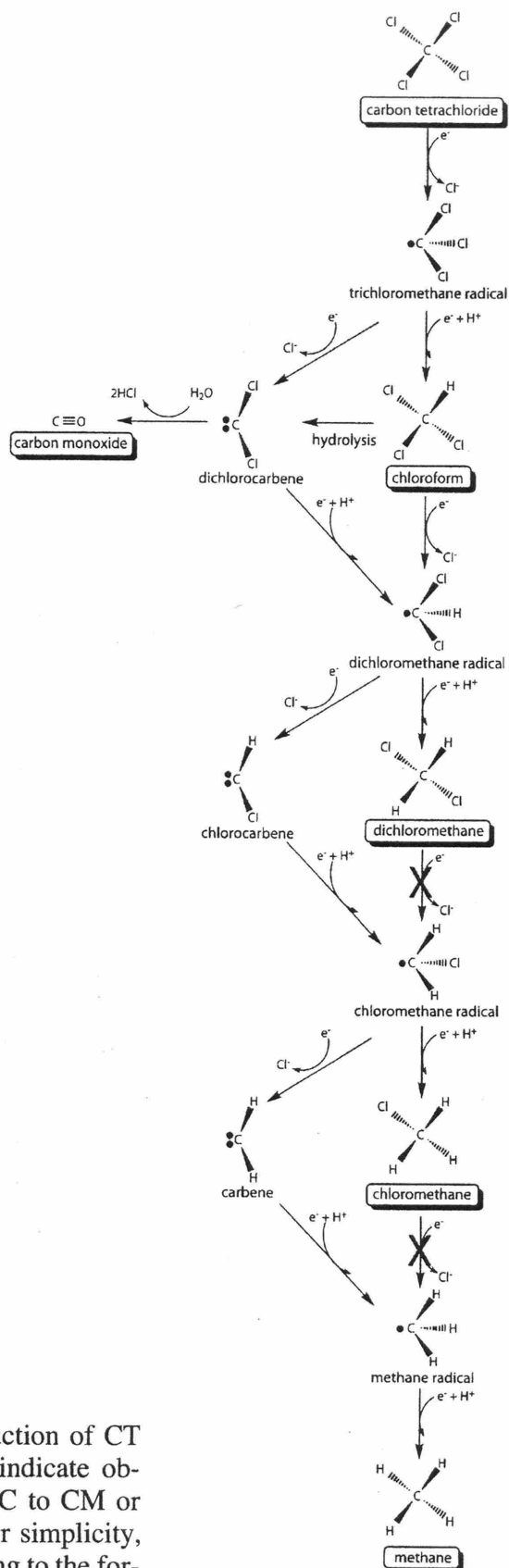

Figure 21.2 Potential reaction scheme for the reduction of CT and CF to CO, DCM, CM, and methane. Boxes indicate observed intermediates/products. The reduction of MC to CM or methane and CM to methane was not observed. For simplicity, reactions of carbenes with water and pathways leading to the formation of coupling products (C_2-C_4 alkanes and alkenes) are not shown.

tems [48]; however, coupling products were not observed during the reduction of acetylene by Zn^0 [29] or vitamin B_{12} with Ti^{III} citrate [36].

Chlorinated Ethenes. Vinyl chloride was readily reduced via hydrogenolysis to ethene, which was further reduced to ethane. No coupling products were observed, and ethene and ethane accounted for nearly all of the carbon introduced as VC. The vicinal dichloroethenes c12DCE and t12DCE were reduced to ethene, ethane, and minor amounts of C_3-C_6 hydrocarbons. Acetylene and VC were observed as intermediates, indicating that the initial reduction of both 12DCE isomers occurs by both hydrogenolysis (forming VC) and β-elimination (forming acetylene); however, the relative significance of each process was isomer specific. Although the reaction rates for c12DCE and t12DCE were quite similar, the maximum yield of VC was 12% for c12DCE but only 0.3% for t12DCE. Moreover, the yields of the coupling products (which were observed during the reduction of acetylene but not VC) were 1.8% for c12DCE and 3.9% for t12DCE, values consistent with the maximum acetylene yields (0.3% and 0.6%, respectively). Thus, reductive β-elimination appears to be more significant for t12DCE than for c12DCE (for which hydrogenolysis was dominant) in our experiments as well as for reduction of these compounds by Fe^0 and Zn^0 [29,48,49].

Reduction of 11DCE resulted in the formation of ethene, ethane, and minor amounts of C_3-C_6 coupling products. Acetylene and VC have been observed as intermediates in 11DCE reduction by vitamin B_{12} (with Ti^{III} citrate as the bulk reductant) [16,36], and VC (but not acetylene or coupling products) is an intermediate in 11DCE reduction by both Fe^0 and Zn^0 [29,48]; however, neither acetylene nor VC was observed as an intermediate in our system.

Although the reductive dechlorination of 11DCE via hydrogenolysis (resulting in the formation of VC) could be considered a likely initial reaction in the reduction of 11DCE to ethene, this does not appear to occur in our system. Figure 21.3 shows a potential reaction scheme for the reduction of 11DCE to ethene (and ultimately ethane). As previously discussed, the initial step in the reduction of halogenated hydrocarbons is commonly reported to be a single electron transfer, with the concerted or stepwise cleavage of the C-Cl bond resulting in the formation of a radical. For 11DCE, this process results in the formation of a VC radical, which is unstable and can react by a number of mechanisms, including 1) accepting a second electron and abstracting a proton to form VC; and/or 2) accepting a second electron with loss of another chlorine to form ethenylidene. Given the rate constant for VC reduction relative to that for 11DCE reduction (Table 21.1), if VC were a significant intermediate in the reduction of 11DCE in our experiments, it would have accumulated to detectable levels. Thus, reduction of 11DCE to ethene via VC is not a significant pathway in our system. A more likely route involves the formation of ethenylidene (which likely would be present as a carbenoid, not a free carbene). Ethenylidene could undergo rearrangement to form acetylene; however, acetylene was not observed as an intermediate. Alternatively, with the transfer of an electron and a proton, ethenylidene could be reduced to an ethenyl radical, that, with an additional transfer of an electron and proton, would form ethene. The net result, the reduction of 11DCE
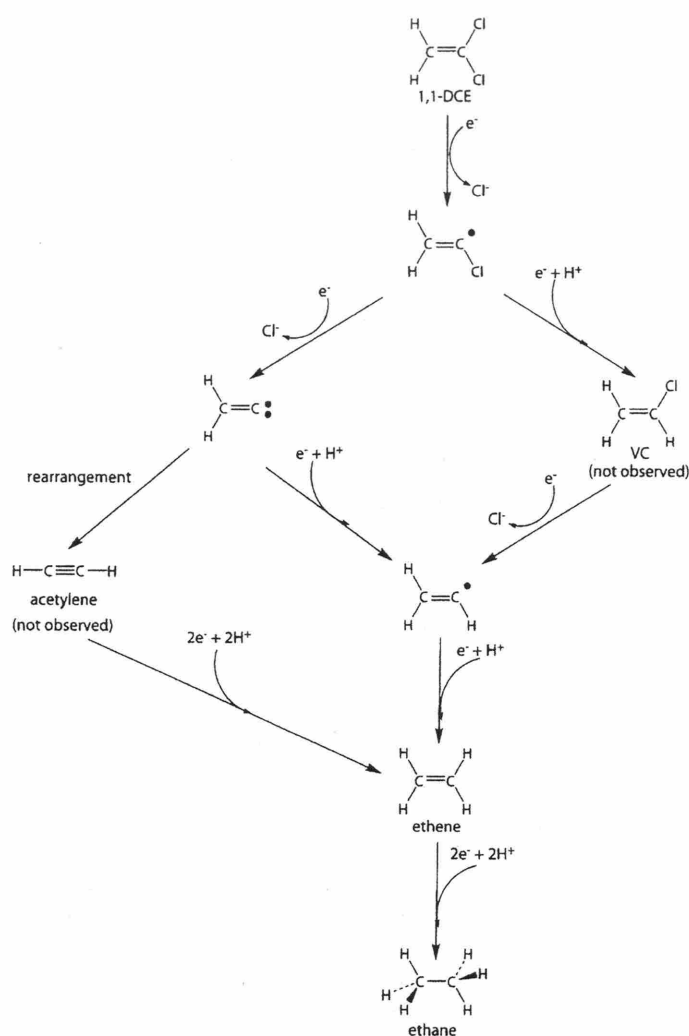
Figure 21.3 Potential reaction scheme for the reduction of 11DCE to ethene and ethane. Acetylene and VC were not observed in our experimental system as intermediates in the reduction of 11DCE mediated by Ni-AHA complexes. The coupling of radical and/or carbene intermediates is not shown. Likewise, this pathway does not show reaction of ethenylidene with the solvent (water).

to ethene via a reductive α-elimination reaction, does not require VC or acetylene as an intermediate. A mechanism of this type was proposed by Arnold and Roberts [48] to explain the kinetics of ethene formation during the reduction of 11DCE by Fe^0. The reaction scheme in Figure 21.3 does not indicate pathways for the formation of the observed coupling products or hydrolysis of ethenylidene to acetaldehyde (which was not measured).

Acetylene, ethene, ethane, and C_3-C_6 hydrocarbons were the only intermediates and products of TCE reduction observed in the experiments with low (5 μmol) initial TCE loading. However, in experiments with initial TCE loadings of 150 μmol, minor amounts of c12DCE, 11DCE, and VC were observed, as well as trace amounts of t12DCE and CAc (in addition to the products mentioned above). These results are consistent with the intermediates and products previously reported for reduction of 16 μmol of TCE mediated by Ni-AHA complexes under similar experimental conditions [28]. The formation of the three DCE isomers as well as CAc indicates that TCE reduction occurs via both hydrogenolysis and reductive β-elimination. Overall, the intermediates and product distribution for TCE reduction mediated by Ni-AHA complexes are similar to those reported for the reduction of TCE by Zn^0 [29], Fe^0 [48], and cobalamin with Ti^{III} citrate [12].

Trichloroethene and ethene were the only intermediates observed during the reduction of PCE at both PCE loadings (5 and 150 μmol), and the final products were ethene, ethane, and C_3-C_6 hydrocarbons. Although TCE was the major chlorinated intermediate observed during the reduction of PCE, no chlorinated intermediates of TCE reduction were detected. However, given the relatively low rate of PCE reduction compared to reduction of TCE and its reduction products (Table 21.1), it is plausible that the intermediates did not accumulate to detectable levels. As with the formation of acetylene from c12DCE and t12DCE, and CAc from TCE, reductive β-elimination of PCE would result in the formation of dichloroacetylene (DCAc). Although DCAc has not been directly observed as an intermediate in PCE reduction, kinetic modeling of the reduction of PCE by Zn^0 and Fe^0 provides indirect evidence for DCAc as an intermediate in PCE reduction by these metals [29,48]. The reduction of DCAc by zero-valent metals (e.g., Zn^0 and Fe^0) is extremely rapid and results primarily in the formation of CAc and t12DCE (and subsequently their daughter products), consistent with its implied role as a highly transient intermediate. In our experiments, a minor peak whose retention time was consistent with the theoretical retention time of DCAc (as predicted on the basis of its boiling point), was observed during PCE reduction in the control systems (Ti^{III} citrate alone and with Ni (but without AHA)). The peak was below an acceptable S/N ratio for reliable confirmation; however, the mass spectrum of this peak was consistent with the expected spectrum for DCAc. Therefore, although the formation of DCAc from the Ni-AHA-me-
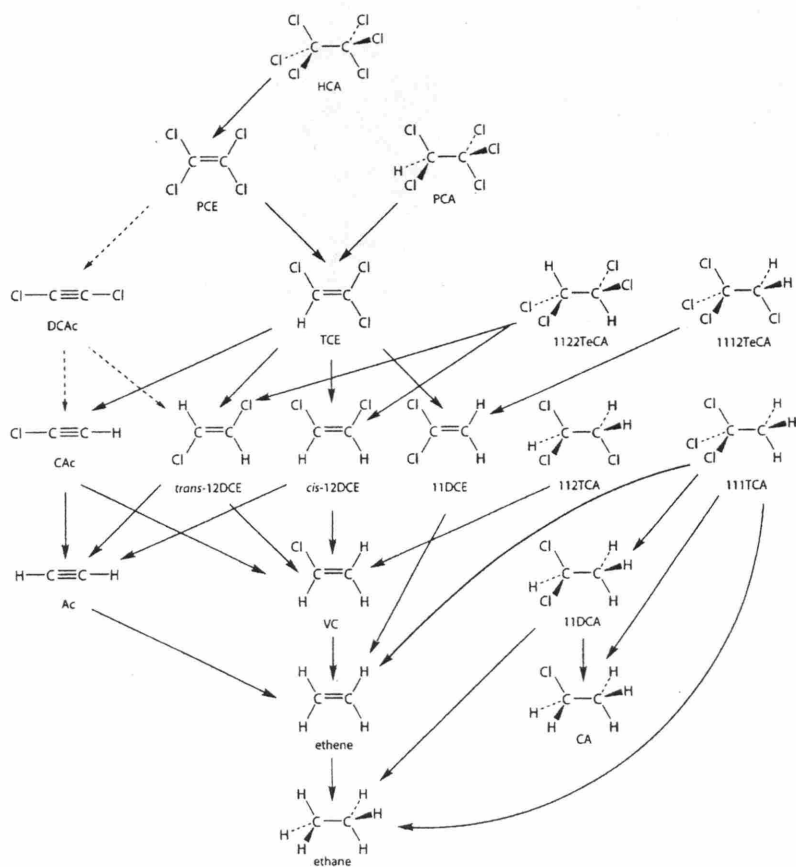

Figure 21.4 Proposed pathways for the reduction of chlorinated ethynes, ethenes, and ethanes mediated by Ni-AHA complexes, with Ti^{III} citrate as the bulk reductant, based on observed products/intermediates. Dashed arrows designate reactions that were not directly observed. Pathways leading to the formation of coupling products (C_3-C_6 alkanes and alkenes) are not shown.

diated reduction of PCE was not directly observed, the tentative identification of DCAc in the controls and the highly transitory nature of DCAc under our experimental conditions suggest that the reduction of PCE to DCAc is likely.

As is evident from the preceding discussion, the reduction of polychlorinated ethenes involves combinations of parallel and serial reactions. Figure 21.4 shows a pathway depicting the relevant reactions for the reduction of chlorinated ethenes. Pathways for formation of coupling products (C_3-C_6 hydrocarbons) are not shown in Figure 21.4 but are discussed later.

Chlorinated Ethanes. No measurable reduction of CA or 12DCA occurred in any of the systems examined over the duration of the experiments (14 d). Reduction of 11DCA was observed only in the presence of Ni-AHA; however, after 72 h, only 8% was reduced, resulting in the formation of ethane and a minor amount of CA. The formation of CA and ethane from the reduction of 11DCA is consistent with a series of sequential hydrogenolysis reactions 11DCA → CA → ethane. However, as mentioned above, CA was not reduced under our experimental conditions, and therefore it is unlikely to be an intermediate in the reduction of 11DCA to ethane. A potential reaction scheme for the reduction of 11DCA to ethane (without CA as an intermediate) is shown in Figure 21.5. As with the reaction schemes proposed for CT and 11DCE, the initial step in 11DCA reduction involves a single electron transfer with the consecutive or concerted cleavage of the C-Cl bond, resulting in the formation of a chloroethane radical. This radical can accept a second electron and a proton, form-
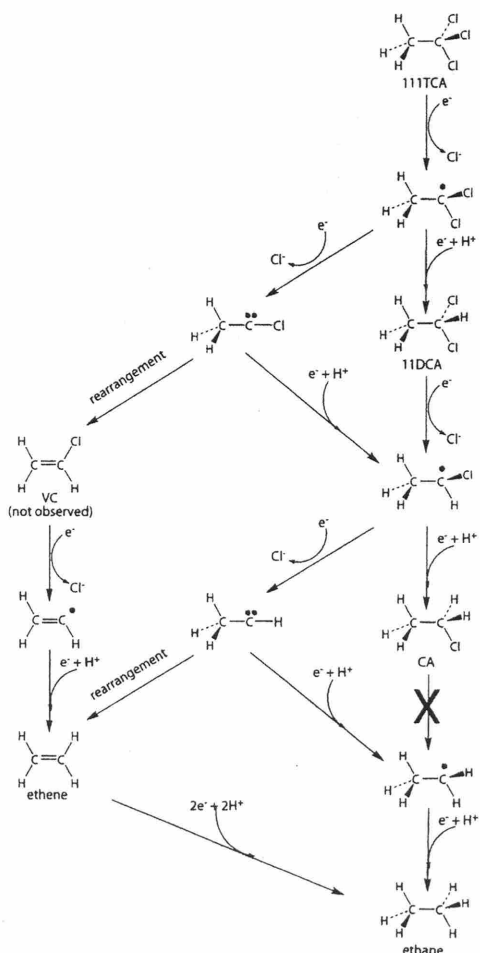

Figure 21.5 Potential reaction scheme for the reduction of 11DCA and 111TCA to ethene and ethane. Chloroethane was not reduced, and VC was not observed as an intermediate in the reduction of 111TCA mediated by Ni-AHA complexes in our experimental system. The coupling of radical and/or carbene intermediates is not shown. Likewise, this pathway does not show reaction of carbenes with the solvent (water).

ing CA and terminating the reaction, or the radical can accept another electron with the release of a second chloride, forming ethanylidene (or the corresponding carbenoid). The rearrangement of this carbene results in ethene. Trace levels of ethene were observed only during the initial hours of 11DCA reduction; however, because the reduction of ethene to ethane is over 100 times faster than the reduction of 11DCA, ethene might indeed be a significant intermediate. In addition to undergoing rearrangement, the carbene might form ethane (without ethene as an intermediate) by the sequential (Figure 21.5) or concerted transfer of two electrons and two protons.

Chloroethane, 11DCA, and ethane were the major products of the reduction of 111TCA, along with minor amounts of ethene and C_3-C_6 hydrocarbons. As with 11DCA, the major products of 111TCA reduction can be accounted for by a series of sequential hydrogenolysis reactions 111TCA → 11DCA → CA → ethane. However, the rates of 11DCA and CA reduction observed independently do not support such a reaction sequence; specifically, CA is not reduced, and the kinetics of 11DCA reduction do not account for the observed rates of CA and ethane accumulation. A reaction scheme consistent with the observed products and kinetics of 111TCA reduction in our system is shown in Figure 21.5. For 111TCA, a single electron transfer with the stepwise or concerted cleavage of a C–Cl bond results in the formation of a dichloroethane radical. The transfer of another electron and a proton to this radical forms 11DCA, which can react further, as described previously. Transfer of a single electron to the dichloroethane radical and loss of chloride results in chloroethanylidene (or its corresponding carbenoid). Rearrangement of chloroethanylidene gives VC, which subsequently is reduced to ethene and ultimately to ethane. However, we did not observe VC during the reduction of 111TCA, suggesting that this is not a significant pathway. Alternatively, chloroethanylidene can accept an electron and a proton, forming a chloroethane radical. As previously discussed, the chloroethane radical might react further, forming CA or the corresponding carbene/carbenoid (which ultimately results in ethene and ethane). The reaction scheme in Figure 21.5 is based primarily on a series of single electron transfers in which an α-haloethyl radical is reduced (with the loss of chloride) to the corresponding carbene. The carbene undergoes rearrangement or is reduced (with a proton transfer) to an ethyl radical containing one less chlorine. If the radical is chlorinated, the cycle can continue. Castro and Kray [40] proposed this type of process to explain the kinetics and product distributions observed during the reduction of geminal halides (including 111TCA) by Cr^{II} in aqueous solution. This reaction scheme was also invoked by Fennelly and Roberts [50] to explain the kinetics and product formation observed with the reduction of 111TCA by Fe^0. The reaction scheme in Figure 21.5 does not depict reactions for the hydrolysis of chloroethanylidene and ethanylidene to acetaldehyde and ethanol (which were not measured), respectively.

The remaining chlorinated ethanes are vicinal halides and as such are susceptible to reductive β-elimination, forming the corresponding chlorinated ethene. Indeed, the only products observed from the initial reduction of 112TCA, 1112TeCA,

1122TeCA, PCA, and HCA were VC, 11DCE, c12DCE/t12DCE, TCE, and PCE, respectively. Moreover, hydrogenolysis, α-elimination, and dehydrohalogenation reactions, which have been observed as pathways for the dechlorination of vicinal chloroethanes under certain conditions [51-53], were not significant for these compounds in our system. The observed intermediates and final products were consistent with the daughter products observed from chlorinated ethene reduction, as described in the previous section. A pathway showing the various parallel and serial reactions involved in the reductive dechlorination of chlorinated ethanes and daughter products is given in Figure 21.4.

Coupling Products. Compounds with carbon chains longer than the parent material are often identified as products of halogenated hydrocarbon reduction by reduced transition metal species [28,50,54-57], and they are generally attributed to radical coupling reactions [50,54,56,57]. Coupling products accounting for 2% to 22% of the carbon introduced as parent compounds were observed during the reduction of Ac, CAc, and all reducible polychlorinated hydrocarbons examined in this study with the exception of 11DCA. Ethene and ethane were the dominant coupling products observed from the reduction of CF and CT, with lesser amounts of propane, propene, *n*-butane, 1-butene, and *cis* and *trans*-2-butene. For the C_2 hydrocarbons the majority (87% to 97%) of the coupling products were the C_4 hydrocarbons *n*-butane, 1-butene, and *cis*- and *trans*-2-butene, with the remainder consisting of methane, propane, propene, and C_5 and C_6 alkanes and alkenes. Coupling products were observed only in systems containing both a reductant (Ti^{III} citrate) and an appropriate parent compound (i.e., CF, CT, acetylene, CAc, or polyhalogenated ethene or ethane). Conversely, coupling products were not observed in systems containing Ti^{III}, Ti^{III} + Ni, Ti^{III} + AHA, or Ti^{III} + Ni + AHA to which an appropriate parent compound was not added, suggesting that the coupling products are derived from intermediates in the reduction of the parent compound and not from other C-containing compounds in these systems [58,59].

Formation of the proposed radical and carbene intermediates in Figures 21.2, 21.3 and 21.5 suggests a number of processes for the formation of C_2-C_6 hydrocarbons, including the coupling of radicals, the coupling of carbenes, and carbene insertion into C-H bonds. Although alkyl radicals have very short lifetimes, they may be stabilized by complexation with transition metals, thereby increasing the probability of radical coupling reactions [60]. The coupling of potential radical intermediates resulting from the reduction of CT and CF (Figure 21.2) could result in the formation of ethane and a suite of chlorinated ethanes ranging from CA to HCA. Coupling of radical intermediates likely to form during the degradation of polychlorinated ethenes would result in polyhalogenated 1,3-butadienes, while coupling of 11DCA and CA radicals from the reduction of 111TCA would form 2,2,3,3-tetrachloro-, 2,2,3-trichloro- and 2,3-dichlorobutane. Although no chlorinated coupling products were measured in our study, the observed C_2-C_4 hydrocarbons are plausible products of their partial reduction or from coupling of nonchlorinated radicals (i.e., methyl, ethyl, and ethenyl radicals).

Coupling of carbenes typically is considered to be unlikely, largely because of

their highly reactive nature and the correspondingly low probability of two carbene molecules interacting, as well as rapid dimer dissociation resulting from high excess internal energy [61,62]. Although these limitations are consistent with conditions in vapor-phase reactions, in our experimental system the proposed carbene intermediates would likely exist not as free carbenes but as transition metal organocomplexes (carbenoids), which may increase their relative stability. Moreover, the presence of solvent molecules also offers a means of dissipating the excess internal energy of potential coupling products, lowering the likelihood of dissociation and increasing the opportunity for carbene-coupling reactions. Indeed, several studies have suggested that carbene coupling does occur in systems that promote the stability and/or physical proximity of carbenes/carbenoids [63-66]. The proposed reaction schemes for CF, CT, 11DCE, and 111TCA (Figures 21.2, 21.3 and 21.5) involve carbene/carbenoid intermediates. The coupling of these species could form products that, on further reduction, yield C_2 and C_4 hydrocarbons, consistent with the observed products. Note that coupling products were not observed during the reduction of 11DCA, suggesting that coupling of ethanylidene was not significant. The formation of C_2-C_4 hydrocarbons from the reduction of chlorinated methanes and C_3-C_6 hydrocarbons from chlorinated C_2 hydrocarbons might also have been the result of carbene insertion into C-H bonds of smaller-chain hydrocarbons (for example, ethane + carbene $\rightarrow$ propane).

Several transition metal complexes (including Ni complexes) are known to promote the coupling of acetylene [67], resulting in the formation of vinyl acetylene (VAc). Vinyl acetylene was not measured in our experiments; however, the C_4 coupling products observed during the reduction of acetylene (butene isomers and n-butane) are consistent with expected daughter products from the incomplete reduction
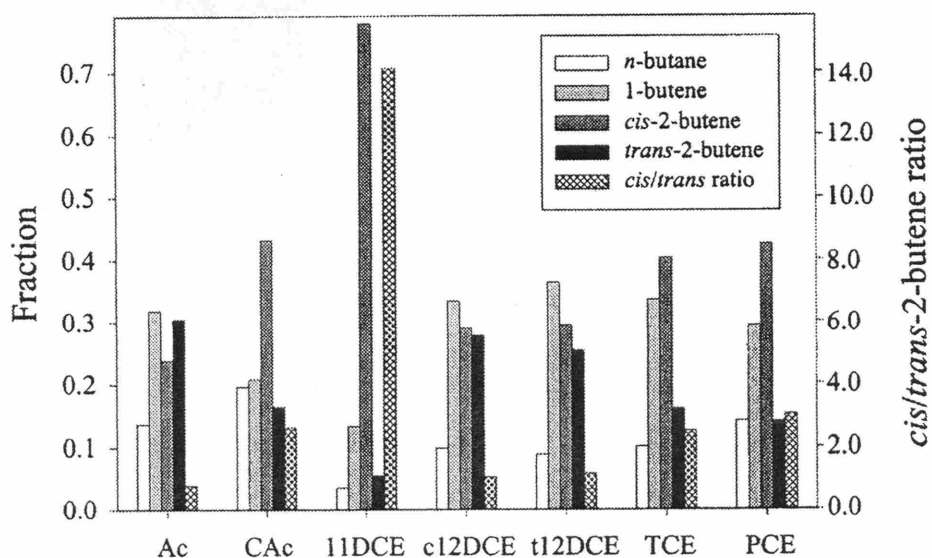

Figure 21.6 Profiles of C_4 coupling products observed during the reduction of acetylene (Ac), CAc, DCE isomers, TCE, and PCE, with the respective ratios of cis-2-butene to trans-2-butene. The fractions of individual C_4 products are relative to the total mass of C_4 products. The C_4 distribution for 111TCE is not shown because of an inability to resolve the peaks for cis-2-butene and CA.

of VAc. The C_4 coupling products produced during acetylene reduction were also observed as products of CAc and polychlorinated ethene reduction. Moreover, acetylene was an observed or theoretical intermediate in the reduction of CAc and the polychlorinated ethenes. However, the differences in the C_4 product profiles of acetylene, CAc, and the polychlorinated ethenes (Figure 21.6) suggest that they are not solely the products of acetylene coupling and that other mechanisms must be involved (particularly in the case of 111TCA, for which acetylene is not a plausible intermediate). This point is best illustrated by the differences in the ratios of *cis*- and *trans*-2-butene. Independent experiments showed that 1-butene is reduced to *n*-butane over the time scale of these experiments, while the 2-butene isomers are not reduced.

Although additional experiments are needed to identify specific intermediates and pathways for coupling products observed in this study, the C_4 profiles for acetylene, CAc, and the polychlorinated ethenes (Figure 21.6) might suggest the relative significance of specific intermediates in the reduction of PCE, TCE, and the DCE isomers. In particular, the high *cis*- to *trans*-2-butene ratios (*c:t*) for PCE and TCE, relative to c12DCE and t12DCE, are consistent with the previously noted roles of CAc and 11DCE (which have comparatively high *c:t* ratios). Likewise, the *c:t* ratios for c12DCE and t12DCE are similar to that of acetylene, an intermediate in their reduction to ethane.

21.3.3. Mechanistic Considerations

A number of organo-Ni complexes are effective agents for the reductive dehalogenation of halogenated hydrocarbons, including 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetra-decane nickel (Ni(tmc)) [38,54], nickel octaethylisobacteriochlorin (NiOEiBC) [57], and coenzyme F_{430} [15,17], a Ni porphinoid found in all methanogenic bacteria. Indeed, it has been suggested that coenzyme F_{430} is involved in the reductive dehalogenation of chlorinated hydrocarbons by methanogenic bacteria [68-71]. The reduction of halogenated hydrocarbons by organo-Ni complexes proceeds by reduction of the Ni^{II} complex to the corresponding Ni^{I} complex by a suitable bulk reductant. Typically, the Ni^{I} complex reduces a halogenated aliphatic hydrocarbon through a single electron transfer and the stepwise or concerted loss of a halide, resulting in the formation of the corresponding Ni^{II} complex and an alkyl or alkenyl radical (as either a free radical or a radical organo-Ni complex) that is further
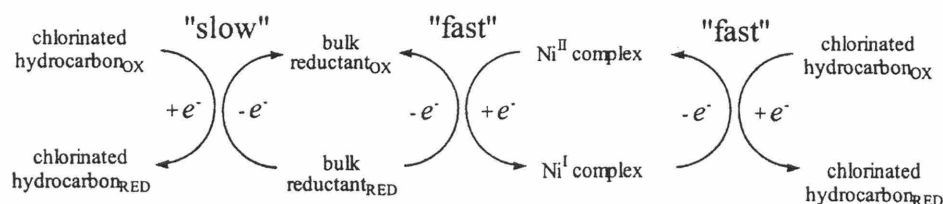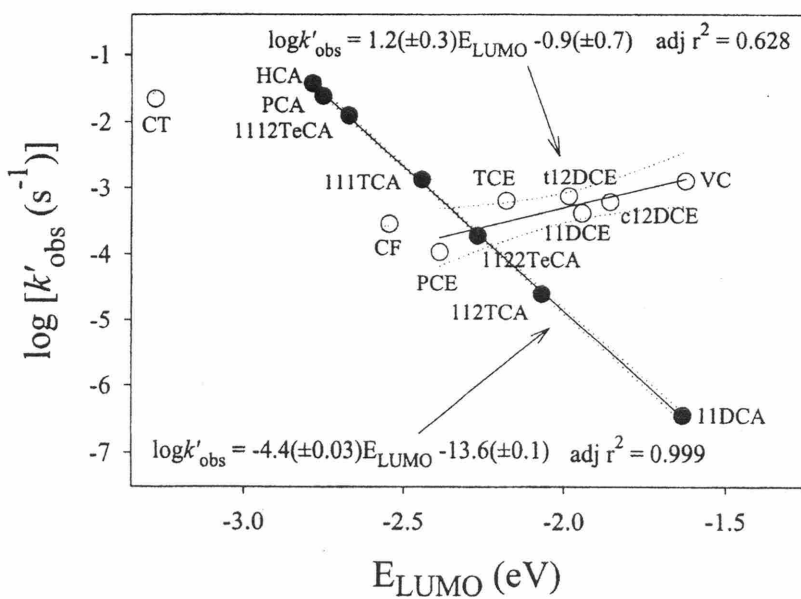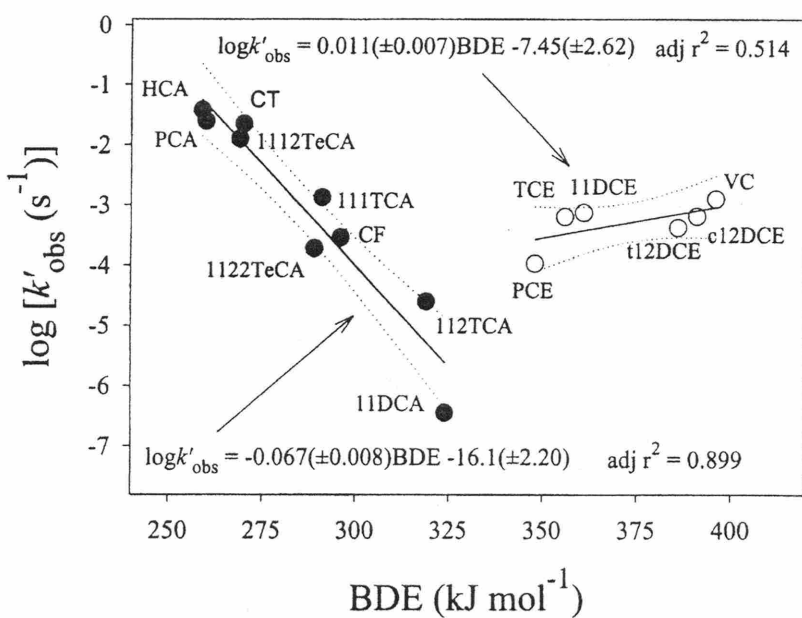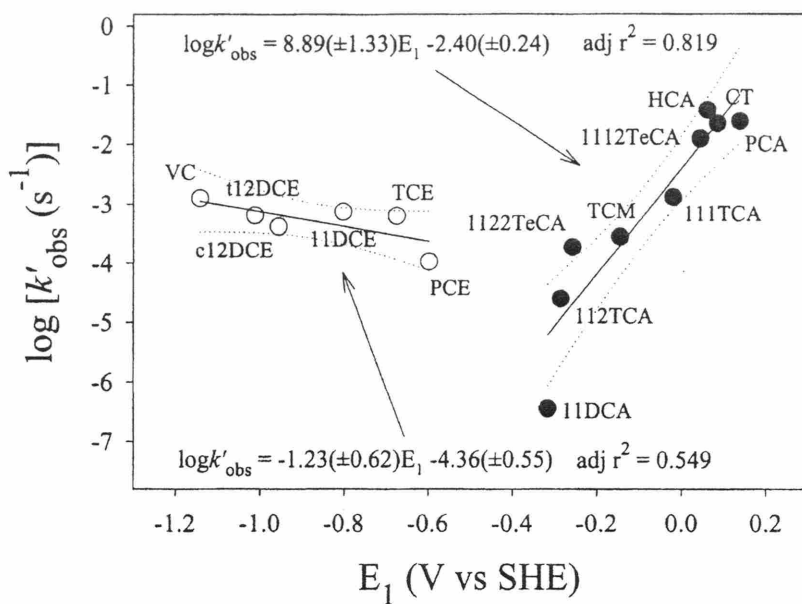

Figure 21.7 Proposed role of organo-Ni complexes as electron mediators in the reduction of chlorinated hydrocarbons.

reduced by a second Ni^I complex. In the presence of additional bulk reductant, the Ni^I complex can be regenerated, thus allowing the Ni complex to act as an electron shuttle or mediator for the reaction (Figure 21.7); such is the case for the reduction of chlorinated hydrocarbons mediated by coenzyme F_{430} with Ti^{III} citrate as the bulk reductant [15,17]. The enhanced reduction of chlorinated hydrocarbons observed in our systems containing Ni^{2+} and AHA, in which Ni-AHA complexes have been identified by Ma et al. [26] as the probable active mediator species, may involve a redox cycling of Ni analogous to that discussed above for coenzyme F_{430}. However, attempts to identify Ni^I species in our system by electron paramagnetic resonance (EPR) spectroscopy were inconclusive because of the masking of any potential Ni^I signal by a broad, intense Ti^{III} peak.

The initial step in the reduction of halogenated hydrocarbons by transition metal species is commonly reported to be a single electron transfer with the stepwise or concerted loss of chloride, resulting in the formation of a radical [39-42]. Indeed, this appears to be the case for chlorinated hydrocarbon reduction by Ni^I organocomplexes [38,57]. For reduction reactions that occur by means of an outer-sphere single electron transfer mechanism, the initial electron transfer is often rate-limiting [72]. Thus, one might reasonably expect good correlation between the reaction rates and one-electron reduction potentials (E_1). These potentials can be determined experimentally or calculated from thermodynamic data; however, significant complications are associated with direct experimental determination of E_1 values, and E_1 values estimated from thermodynamic parameters are limited by the quality of the thermodynamic database [73]. Many researchers have used the homolytic C-Cl bond dissociation energy (BDE) or the energy of the lowest unoccupied molecular orbital (E_{LUMO}) as surrogates for E_1 [73-77]. For reductive dechlorination reactions, the homolytic BDE refers to the energy required to dissociate C-Cl to C· and Cl·, and as such it reflects the ease of radical formation. The LUMO is the frontier molecular orbital into which electron transfer takes place; consequently, E_{LUMO} is directly related to the electron affinity of the molecule, and thus the energy of this orbital is a significant component of the overall driving force of the reaction.

The relationships between the observed pseudo-first-order rate constants for the reduction of chlorinated methanes and ethanes mediated by Ni-AHA complexes and E_1, BDE, and E_{LUMO} show clear differences between the chlorinated alkanes and alkenes (Figure 21.8; values for E_1, BDE, and E_{LUMO} are from Totten and Roberts [73]). The data show distinct differences between the linear free-energy relationships

Figure 21.8 Observed pseudo-first-order rate constants (k'_{obsd}) for the reduction of chlorinated methanes, ethanes, and ethenes mediated by Ni-AHA complexes versus one-electron reduction potentials (E_1), C-Cl bond dissociation energies (BDE), and the energy of the lowest unoccupied molecular orbitals (E_{LUMO}). E_1 values for the most thermodynamically favorable product were used. Values for E_1, BDE, and E_{LUMO} are from Totten and Roberts [73]. Dotted lines indicate 95% confidence intervals. Numbers in parentheses are ± the standard error of the preceding term.

Top panel:

$\log k'_{obs} = 8.89(\pm 1.33)E_1 -2.40(\pm 0.24)$ adj $r^2 = 0.819$

$\log k'_{obs} = -1.23(\pm 0.62)E_1 -4.36(\pm 0.55)$ adj $r^2 = 0.549$

X-axis: E_1 (V vs SHE)
Y-axis: $\log [k'_{obs}$ (s^{-1})]

Labels: HCA, CT, 1112TeCA, PCA, VC, t12DCE, TCE, c12DCE, 11DCE, PCE, 1122TeCA, TCM, 111TCA, 112TCA, 11DCA

Middle panel:

$\log k'_{obs} = 0.011(\pm 0.007)BDE -7.45(\pm 2.62)$ adj $r^2 = 0.514$

$\log k'_{obs} = -0.067(\pm 0.008)BDE -16.1(\pm 2.20)$ adj $r^2 = 0.899$

X-axis: BDE (kJ mol^{-1})
Y-axis: $\log [k'_{obs}$ (s^{-1})]

Labels: HCA, CT, PCA, 1112TeCA, 111TCA, CF, 1122TeCA, 112TCA, 11DCA, TCE, 11DCE, VC, t12DCE, c12DCE, PCE

Bottom panel:

$\log k'_{obs} = 1.2(\pm 0.3)E_{LUMO} -0.9(\pm 0.7)$ adj $r^2 = 0.628$

$\log k'_{obs} = -4.4(\pm 0.03)E_{LUMO} -13.6(\pm 0.1)$ adj $r^2 = 0.999$

X-axis: E_{LUMO} (eV)
Y-axis: $\log [k'_{obs}$ (s^{-1})]

Labels: CT, HCA, PCA, 1112TeCA, 111TCA, TCE, t12DCE, VC, CF, 11DCE, c12DCE, PCE, 1122TeCA, 112TCA, 11DCA

(LFERs) for chlorinated alkanes and alkenes. The correlation between k'_{obs} and E_1 is fairly robust for the chlorinated alkanes and consistent with their expected relationship; that is, there is a general trend of increasing reaction rate with increasing one-electron reduction potential. Similarly, the reaction rates for the chlorinated alkanes decrease as the energy for homolytic C-Cl bond dissociation increases. However, the best correlation is observed between k'_{obs} and E_{LUMO} for the chlorinated ethanes. Carbon tetrachloride and CF are outliers, an observation that might indicate subtle differences in the relationship between k'_{obs} and E_{LUMO} with regard to chlorinated methanes and ethanes. Though they are not proof of a particular reaction mechanism, the results of these LFERs are consistent with a single electron transfer as the rate-limiting step for the Ni-AHA-mediated reduction of chlorinated ethanes.

The correlations between k'_{obs} and E_1, BDE, and E_{LUMO} are far less robust for the chlorinated ethenes (Figure 21.8). Moreover, the correlations between k'_{obs} and E_1, BDE, and E_{LUMO} are of substantially lower magnitude and are the inverse of those observed for the chlorinated ethanes; that is, reaction rates decrease with increasing E_1 and increase with increasing BDE, E_{LUMO}, and extent of chlorination. For example, the reduction of VC was faster than that of PCE. This observation is counter to the commonly observed trend of faster reduction of chlorinated hydrocarbons with increasing extent of chlorination [13,29,77, and many others]. However, the reverse trend (increasing reduction rate with decreasing chlorination) has been observed for the reduction of chlorinated ethenes by Fe^0 [48] and FeS [78]. The reatively poor correlation between k'_{obs} and E_1, BDE, and E_{LUMO}, and the decrease in reaction rate with increasing extent of chlorination suggest that the rate-limiting step for the Ni-AHA-mediated reduction of chlorinated ethenes involves factors other than single electron transfer. Additional research is required to fully elucidate the reaction mechanism(s) in this system.

21.4. CONCLUSIONS

Nickel-AHA complexes are capable of acting as electron mediators in the reductive dechlorination of a wide range of C_1 and C_2 chlorinated hydrocarbons, nearly all of which are U.S. Environmental Protection Agency Priority Pollutants. Chlorinated solvents such as CT, CF, PCE, and TCE have been used in many industrial and commercial applications, and the improper use and disposal of these materials has resulted in widespread surface and subsurface contamination. The reduction of chlorinated hydrocarbons *in situ* (and in some engineered systems) is often incomplete and may result in the accumulation of less chlorinated daughter products that pose a greater environmental hazard than the parent compound. For example, TCE may be reduced to VC, a known carcinogen. The Ni-AHA-mediated reduction of most of the chlorinated hydrocarbons examined in this study was relatively rapid (with half-lives typically less than 1 h under our experimental conditions) and generally resulted in nonchlorinated products; thus, HS-transition metal complexes might have potential applications for the remediation of chlorinated hydrocarbons and other contaminants.

Although Ti^{III} citrate is not representative of the reductants typically found in natural suboxic and anoxic environments (for example, reduced iron and sulfur species, among others) and nickel generally is not present in most natural systems at the concentrations used in our experiments, the ability of Ni-AHA complexes to act as electron mediators for the reduction of chlorinated hydrocarbons by Ti^{III} citrate suggests that HS-transition metal complexes are effective electron transfer agents in natural systems. Indeed, DOM-metal complexes have been suggested to contribute to the reduction of substituted nitrobenzenes by hydrogen sulfide under acidic conditions [10]. However, additional research is needed to evaluate the overall significance of the activity of HS-metal complexes as electron mediators for redox reactions in natural systems.

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